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A SURVEY OF FIRE-PREVENTION PROBLEMS IN CLOSED OXYGEN-CONTAINING ENVIRONMENTS

by

Valentine D. Galasyn
Lieutenant, MC, U. S. Navy

Bureau of Medicine and Surgery, Navy Department
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Released by:

Gerald J. Duffner, CAPT MC USN
COMMANDING OFFICER
U. S. Naval Submarine Medical Center

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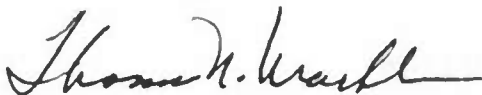
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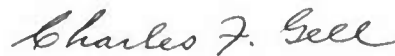
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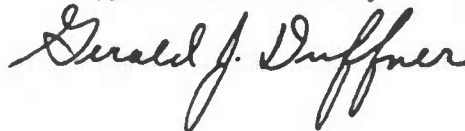
Thomas N. Markham, LCDR MC USN
Head, Military Operations Branch
SubMedResLab

Reviewed and Approved by:



Charles F. Gell, M.D., D.Sc.
Scientific Director
SubMedResLab

Approved and Released by:



Gerald J. Duffner
CAPTAIN, MC, U. S. NAVY
COMMANDING OFFICER, SMC

SUMMARY PAGE

THE PROBLEM

To review the scientific literature concerning fire hazards in hyperbaric chambers and oxygen-enriched environments.

FINDINGS

A careful review of medical, engineering and fire prevention literature has been performed to determine the fire risk factors associated with these environments. A comprehensive bibliography is included.

APPLICATIONS

In the construction, remodeling or operation of hypo and hyperbaric chambers the principles of fire prevention and safety are of paramount importance. The factors outlined here will assist in identifying the areas which require special consideration.

ADMINISTRATIVE INFORMATION

This investigation was conducted as a part of Bureau of Medicine and Surgery Work Unit MF011.99-9003—Physiological Effects of Long Duration Habitation in Hyperbaric and Artificial Environments. The present report was approved for publication on 20 May 1968 and has been designated as Submarine Medical Center, Submarine Medical Research Laboratory Report No. 526. This is Report No. 3 on the Work unit listed above.

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ABSTRACT

The problem of fire ignition and flame propagation in oxygen-containing or oxygen-enriched environments is dependent upon both the percentage of oxygen, oxygen partial pressure, and presence of the diluent inert gas. Oxygen percentage is the single most important feature and its effect is most striking in concentrations greater than 42%. The diluent gas affects the initial combustion temperature and the rate of propagation. Helium requires a higher ignition temperature, but produces an increased spread; while nitrogen requires a lower ignition temperature, but shows a decreased propagation rate. The most effective extinguishment system employs a hand-held, high-pressure, water hose. However, specific prevention measures are mandatory when dealing with these environments.

A SURVEY OF FIRE PREVENTION PROBLEMS IN CLOSED OXYGEN-CONTAINING ENVIRONMENTS

INTRODUCTION

The problem of fire in a closed oxygen-containing environment is very real and vitally important, as evidenced by several disastrous fires in recent years. Foremost among these was the Apollo accident on 27 January 1967 in which three astronauts were killed. Four days later two airmen lost their lives in the oxygen-rich chamber of a space cabin simulator at Brooks Air Force Base, Texas. However, these two tragedies do not stand alone as examples of fires in oxygen-enriched environments.

In 1945 a spark from a ventilating fan caused a fire in a recompression chamber aboard a Navy diving ship which claimed two lives. Twenty years later, a fire in a missile silo took the lives of 53 workmen when a high-pressure hydraulic line ruptured and accidentally struck a welding rod (20). On 15 February of the same year another fire occurred in a Naval recompression chamber, claiming still two more lives. The latter incident occurred at the Naval Experimental Diving Unit, Washington, D. C., while an artificial atmosphere of oxygen, helium and nitrogen was being used.

After conducting an extensive investigation into the Experimental Diving Unit fire, Harter (23) fixed the cause as the malfunction of a portable carbon dioxide scrubber within the chamber. In order to conserve the expensive atmosphere, this scrubber was employed in lieu of venting the chamber to control carbon dioxide accumulation. The fire, which started as a small flame in the scrubber and then flashed throughout the lock, was initiated by local heat generated by the motor. Other possibilities, such as open flame ignition, static sparking, heat generated by adiabatic compression, and electric arcing were considered and discounted. In addition to the deaths, untreated terry-cloth bathrobes were consumed, untreated mattresses charred, and wiring insulation and rubber tubing destroyed. Harter

summarized present knowledge concerning fire hazards in oxygen-containing atmospheres at varying pressures. He pointed out that flammability of material is enhanced by increasing the pressure of gas mixture at constant composition, and that the use of inert gases with lowered thermal conductivity causes lower ignition temperatures. Those with higher thermal conductivity raise ignition temperatures. He emphasized the need to learn more about the effects of inert gases on ignition and burning in closed chambers. He also discussed safety procedures, proper design of electrical systems, the selection of nonflammable and flame-resistant materials, and the importance of developing automatic rapid detection and fire extinguishment systems.

Denison, at the Royal Air Force Institute of Aviation Medicine, has studied in great detail the fire hazards present in O₂-rich environments at varied pressures (15, 16, 17). His observations showed that the spark energies required to ignite common clothing materials may be decreased more than 1000-fold in pure oxygen at one atmosphere and the rate of burning increased about 5-fold. Conventional flame-proofed fabrics, paints, lubricants and insulating materials burn vigorously in 30-40% oxygen, and smothering is an ineffective means of fire extinguishment in oxygen. According to Denison, the principles of reducing fire risks include minimal use of potential ignition sources (hot surfaces and electrical, electrostatic, and mechanical sparking), minimal use of flammables (clothing, bedding, paint, rubber, wiring insulation, lubricants, activated charcoal), separation of potential ignition sources and flammables, use of fire-warning devices (heat, flame and smoke detection), use of flame traps where possible, effective means of extinguishing fires, clearly understood safety regulations, and adequate fire drills.

In experiments with mannikins and dead pigs to determine what would happen to a

man in the first minute of a fire in an atmosphere of pure oxygen, Denison found that without protection fatal injury occurred within a few seconds of ignition, due to an initial flashover of flame propagated by both the rays of untreated clothing and skin hair, followed rapidly by generalized burning. Clothing fire-proofed with borax/boric acid reduced rate of flashover and spread of fire, as did reduction of oxygen partial pressure. High-density water sprays and hand-held hoses were the most effective in extinguishment. In order to avoid fatal damage, the water spray had to be initiated within a few seconds.

The phenomenon of flashover has been investigated by Waterman (39). He used a test chamber in which he could simulate typical rooms of a house under ordinary atmospheric conditions. Among his conclusions he stated that room flashover occurs because the ignition energies of combustible contents confined to a room are exceeded almost simultaneously. The ignition energies depend on a rate of heating and O_2 content of available air. Flashing over the ceiling of a room is due primarily to the constraining effect of the ceiling on the flames arising from the initiating item and not from accumulation of unburned gases near the ceiling.

BURNING RATES

Numerous recent investigations have been concerned with the combustibility of various materials in controlled environments, and with the production of materials that are fire-resistant under extreme conditions. Earlier observations that a decrease in percentage of diluent inert gas, such as nitrogen, led to an increased burning rate of solid organic substances led Clamman (7,8) to a study in which he burned cigarettes in O_2 , O_2-N_2 , and O_2-He atmospheres at varying pressures. He found that a cigarette in air at one atmosphere ($pO_2 = 160$ mm. Hg.) burned in about $3\frac{1}{2}$ minutes, while in pure oxygen at 160 mm. Hg. it burned in about 1 minute. In the various gas mixtures used, the burning time increased as pressure was decreased, as expected, but not linearly. The presence of diluting gases prolonged the burning time. He also

found that a helium-oxygen mixture containing 21-25% O_2 suppressed combustion within a pressure range of 760 to 400 mm. Hg. Lorentzen (32) has observed the change in size of a candle flame with varying percentage and varying partial pressure of oxygen. When he decreased pO_2 gradually, keeping the percentage of oxygen constant at 20.93%, the flame size also decreased gradually until it was extinguished at 15-20 mm. Hg. When he maintained one atmosphere pressure and decreased the percent of oxygen by diluting with N_2 , the decrease in flame size was more abrupt. At 16 percent oxygen the flame was extinguished. Sixteen percent O_2 at 760 mm. Hg. corresponds to the partial pressure of O_2 with 20.9% O_2 at 584 mm. Hg. Thus the size of the flame, and burning rate, is more dependent on the percent of oxygen than on its partial pressure.

Cook et al (13) have studied ignition temperatures and burning rates under varying conditions. They burned paper strips held at a 45° angle in 26 different gas mixtures at pressures ranging from 0.21 to 10.1 atmospheres. Ignition temperatures decreased with pressure increase. The burning rate of the strips increased non-linearly as oxygen partial pressure and percentage oxygen increased. Ignition was more difficult with helium as the diluent, as compared to nitrogen. Yet at pressures up to seven atmospheres, the burning rate with helium as the diluent was usually higher than with nitrogen. These findings are attributable to the higher heat conductivity of helium. Cook pointed out that, even though the burning rate is higher in helium, the advantages of helium over nitrogen as an oxygen diluent are: (1) more difficult ignition of flammable materials, (2) the less dense mixture is easier to breathe at high pressures, and (3) helium has no narcotic effect on divers down to 600 feet of sea water.

Hall and Fang (22) have studied the ignition temperature and rate of burning of paper strips in the five pounds per square inch (psi) absolute oxygen atmosphere being used in space cabins. Comparing this condition with air at one atmosphere, there was a lowered ignition point and six-fold increase in

burning rate. Other substances tested included neoprene-coated nylon twill, light weight nylon, and vinyl plastic. These all melted under the control conditions but ignited in the test atmosphere. In a study of the flammability of spacecraft wire in pure O_2 at 5 psi, Mathes and Frisco (34) tested various insulations which are generally considered to be non-flammable. Only H-film (Dupont's Kapton^(R)) proved to be highly fire-resistant. Most of the materials yielded vapors when heated and caused flaming to occur more readily. Teflon insulation burned only after vigorous heating with an external heat source. Silicone rubber and polyolefin insulation were found to be especially flammable. In a similar study of electrical insulation, Teflon insulation generated pyrolysis products and burned slowly only under extreme electrical overload (35). The flame was self-extinguishing when the overload current was stopped. Further, Raychem's Rayolin-N insulation was found to vaporize and burn with the production of highly noxious fumes.

Bjurstedt and Severin (4) substituted hydrogen instead of helium for nitrogen in deep-diving experiments described in 1948. They pointed out that the explosion risk could be avoided by keeping the O_2 concentrations at four percent or less, and they stressed the advantages of hydrogen as a diluent. Because of its lower molecular weight, inhalational resistance is considerably decreased at high pressure. Further, it is chemically inert when inhaled, and the narcotic effect is felt to be minimal. Kuchta (29) has obtained flammability data for H_2 - O_2 -He mixtures at 100 and 760 mm. Hg., demonstrating that compositions containing as little as five percent oxygen would propagate flame. Apparently, there is no information available on upper limit of flammability for these mixtures at increased pressures.

In one early study at the National Bureau of Standards (33), the flammability of 109 materials used in commercial air transport was determined at ordinary atmospheric conditions. In this study special emphasis was placed on plastics and other synthetic materials. Much of the study was concerned with the establishment of test methods so that ig-

nition time, burning rate, self-extinguishing time, and smoke production could be measured quantitatively. Huggett et al (26) studied the ignition energies and rate of flame spread of various space cabin materials in air, and in 100% O_2 at 258 mm. Hg. Many materials which did not support combustion in air burned vigorously in the oxygen atmosphere. Prolonged exposure to pure O_2 did not change the ignitability of the materials studied. Furthermore, the geometry and surface texture of materials had a profound effect on the rate of flame spread.

Huggett also studied the ignition energies and rates of flame spread in He- O_2 and O_2 - N_2 mixtures (25). These mixtures had been suggested for use in space cabin atmospheres, since the fire hazard in pure oxygen at reduced pressure is so great and flame propagation rates are reduced in the presence of an inert diluent. Confirming Cook's work, he found that, even though more energy was required to ignite materials in He- O_2 than in comparable N_2 - O_2 mixtures, the rate of flame spread is appreciably greater in He- O_2 mixtures. He concluded the fire hazard is greater with helium as diluent. In related work, Johnson et al (27) studied the flammability of fabrics and other solids in He- O_2 and O_2 - N_2 mixtures at increased pressures. Most of the materials tested ignited readily, with the exception of Teflon and glass fabrics. In general, their findings agreed with those of Huggett.

An earlier study of fabrics (10) in oxygen enriched air and compressed air demonstrated the reduced protection offered by commonly used materials of low combustibility such as wool and leather. Impregnating cotton twill with borax/boric acid provided additional limited protection.

The combustibility of three commonly used materials—polyethylene, polyvinyl chloride, and silicone rubber was evaluated by Fisher and Gernstein (18). Ignition temperatures of the first two increased with decreased pressure and decreased oxygen percentage. However, the ignition temperature of silicone rubber was largely independent of these conditions. This is apparently due to chemical reactions and the production of a surface oil on

the specimens prior to ignition. Guter (21) has studied the ignition temperatures of many materials considered for use in high-pressure O_2 systems. Using pressures up to 250 atmospheres, he tested lubricants, natural and synthetic rubber materials, various polymers, valve seat materials, metals and alloys. The general trend was a reduction in ignition temperature with increasing pressure. Teflon, Kel-F polymer, and phosphorylated polyvinyl alcohol were among the most stable non-metallic substances he examined.

The U.S. Bureau of Mines has evaluated the fire hazard of many solid materials under hyperbaric conditions (30). Ignition temperatures and flame propagation rates were determined under air, O_2 and O_2 - N_2 mixtures at different pressures. As expected, ease of ignition and rate of flame spread increased with greater oxygen percentages and increased pressure. Although an effective increase in flame propagation was demonstrated with increased pressure, the most pronounced effect was recorded as a function of the percent oxygen concentration. The increased effect became most striking at higher oxygen percentages (42% or greater). Depending upon the oxidant atmosphere and pressure, some combustible materials like cotton sheeting, ignited at lower temperatures after treatment with Dupont X-12 flame retardant. Fire-resistant Nomex (Dupont) fabric was found to have the highest ignition temperature (600°C in air at 1-3 atm). The ignition energies of various anesthetic gas mixtures were also studied under hyperbaric conditions. For hydrocarbon anesthetic mixtures of constant mixture composition, the values varied inversely with the square of the pressure. The halogenated hydrocarbons anesthetics were found to be the safest.

In yet another study by Cook et al (12), the combustibility of various fabrics used in chambers was determined. Samples were burned in air and in O_2 at various pressures. Since burning rates were found to be highly dependent on the angle at which the specimen was held, each sample was clamped at a 45° angle to provide uniformity. Again, combustion rates increased with increasing pressure and increased oxygen. Terry cloth was found

to be especially hazardous because the nap burned so rapidly. The safest material found was Beta-fiberglas, which showed no sign of combustion. However, this material suffers from reports of skin irritation. Teflon cloth was the next safest. Nomex "High-temperature Resistant" nylon cloth and Roxel flame-retardant cotton were found to be safer than untreated cotton. However, Nomex is capable of generating static electricity in a dry atmosphere. "Ethoquad C-12" (Armour) can be applied at each washing as an antistatic treatment. A detailed study on the burning characteristics of Nomex by Chianta and Stoll (9) involved oxygen concentrations ranging from 30 to 100%, diluted with argon, nitrogen, and helium at gas flow rates that maintained pressures of 14.7, 10.9 and 7.3 psia. The destruction rate of the fabric decreased with decreasing O_2 concentration, and also with decreasing density of the diluent gas. As in other studies, it was found that helium exhibited the greatest damping effect on combustion.

The flammability limits of many combinations of gases and vapors have been published in an earlier Bureau of Mines report (14). A lower and a higher limit of flammability is given for each mixture, the lower limit corresponding to the minimum amount of combustible gas capable of producing flammability of the mixture. The lower limits were found to be nearly the same in oxygen as in air, but the higher limits were much greater in oxygen than in air. Many variables such as ignition source, humidity, pressure as well as size and shape were considered. The effect of pressure was specific for each system, but in general a reduction in pressure narrowed the range of flammability by increasing the lower and decreasing the higher flammability limit.

The ignition of metals in oxygen has been studied extensively (40). The conclusion was that all metals, with the possible exception of gold and platinum, can be expected to ignite in oxygen at some elevated temperature. Alloys of titanium, zirconium, thorium, uranium, lead, tin and magnesium were found to ignite at relatively low temperatures. Alloys of nickel, cobalt, copper, silver, and austenitic

stainless steels were found to be quite stable. Several energy input sources, such as electric spark, stress rupture, explosive shock, and mechanical impact, were found to cause ignition of metals and an increase in the oxygen partial pressure promoted this ignition.

Other materials being developed in an attempt to reduce fire hazards include anti-static synthetic films and ceramic fibers made from silica, alumina, and silica-carbon (1). In the latter group hybrid cellulose-fiber filaments are spun, then ignited and sintered to remove the organic portion.

FIRE PREVENTION

Fire safety in a closed environment involves many factors, of which prevention is the most important. Chamber design and all materials used must be selected with fire safety in mind. It must also be realized that the possibility of fire cannot be completely eliminated, so measures should be taken to remove personnel from the area as fast as possible and to combat any fire which may occur. Brown and Smith (5) have emphasized the importance of fire safety, and have recorded the safety features incorporated into their clinical hyperbaric chamber at Duke University. These include proper electrical wiring and electrical equipment, non-combustible lubricants, fire-retardant paint, conductive silicone rubber hoses, and flame-resistant fabrics such as cotton treated with Tetra-kis (hydroxymethyl) phosphonium chloride. They have utilized an internal air recirculating system to prevent buildup of oxygen pockets, and controlled relative humidity at 60-70% to reduce static sparking. All their expired gases, including anesthetic agents, are vented to the outside by a closed system. They consider the best extinguisher is a water-quench system, including both an overhead spray and separate hoses that can be manned by personnel inside the chamber. Emergency air lines with face masks, supplied by separate air banks, are also placed throughout the chamber. There is an emergency power supply available in the event fire inactivates the main supply. Each compartment of the chamber contains an emergency medical kit.

The special problem of space cabin fire safety, including prevention, detection, and extinguishment, has been presented qualitatively in a report published in 1966 by Geoghegan (19). He summarized the currently available data and presented a literature survey. The limited data on the burning of materials at zero gravity in various oxygen concentrations was presented, and it was pointed out that the only method available for extinguishing such fires was to dump the cabin atmosphere. However, dumping is not suitable below 50,000 feet (launch and re-entry phases). He considers the eventual technique for combatting small zero-gravity fires will involve various types of small hand-held extinguishers.

The explosion hazard created when small amounts of oil are introduced into submarine high pressure air systems has been investigated by Wilson et al (41). Explosions resulted when air was compressed rapidly in the presence of standard compressor lubricants. These explosions were initiated by compression ignition. This study emphasized the importance of maintaining oil-free air pressure systems and avoiding rapid pressurization by using valves that operate slowly.

FIRE DETECTION

The problem of rapid fire detection and coupling with automatic extinguishment systems is being studied intensively. Hill et al (24) and Trumble (38) have worked with hydrogen-air fire detection systems. Hill used the ultraviolet OH band radiation from the flame as the basis for detection, but he found no photomultiplier tube detector to be wholly satisfactory. An ideal detector requires both "solar-blindness" and linearity of response. Infrared flame detectors currently available are not wholly solar-blind, and hence, are not suitable for use. Stevens (37) has also studied the possibility of using an infrared detection system to trigger an automatic fire extinguishing system. He concluded that the power output of present practical detection systems would be too low for automatic activation. Trumble (38) developed a portable detection system, using the ultraviolet radiation band and the

McGraw-Edison type 42262 photomultiplier tube coupled to an optical gain system. He was able to detect a 1-inch high hydrogen-air flame 80 feet away. Campbell and Chang (6) have undertaken the development of solar-blind solid state ultraviolet detectors for use in fire detection systems. They have studied both silicon carbide and aluminum nitride detection systems, and silicon carbide shows the greatest promise as a potential solid state fire detector.

Using thermistors as temperature sensing elements, the U. S. Navy Marine Engineering Laboratory (28) developed a temperature alarm system with an accuracy of $\pm 1^\circ\text{F}$ in the range from 30 to 130°F . This compact system may also be adapted for the monitoring of pressure, humidity, fluid flow or liquid level.

In a recent review of the aircraft fire protection program at the Air Force Aero Propulsion Laboratory, Berry and Botteri (2) reviewed the types of detectors systems under study. These include ultraviolet detectors, aluminum nitride and silicon carbide solid-state detectors, hazardous vapor detectors, a thermo-chemical overheat warning system, and an interesting fiber-optics hazard identification device. In the latter, fiber optics bundles extending to remote parts of an aircraft are used to transmit images and light from flames.

FIRE EXTINGUISHMENT

When planning a fire extinguishing system, the three basic mechanisms involved in extinguishment must be considered. First, cooling below the ignition temperature, as with water; second, smothering to reduce the oxygen or fuel concentration; and third, separating the fuel from the oxidizer mechanically, such as protein foam on jet fuel fires. The final mechanism involves chemical interference with combustion products at the flame front.

Segal (36) has investigated water extinguishment systems, and his work complements that of Brown (5) mentioned earlier. Fires were extinguished most effectively with a flexible hand line. A fixed water spray system, while not as effective, was considered

necessary as a back-up in case the occupants became incapacitated and could not operate the hand lines. Another study (11) on the cooling effectiveness of various systems has shown straight stream water most effective, with water-fog less effective. Botteri (3), in discussing fire protection in oxygen enriched atmospheres, concluded, on the basis of fire-suppressant capability and compatibility with personnel, that water and DuPont's Freon FE 1301 (CBrF_3) are the best extinguishing agents available. He stated that extinguishment systems should be connected to alarm systems for automatic operation, and that alarm systems will probably include ultraviolet, infrared, and smoke particle detectors.

Freon FE 1301 is a liquified compressed gas boiling at -72°F . It has been tested as an agent against Class A (solid cellulosic materials), Class B (flammable liquid), and Class C (electrical) fires. It has been found more effective than carbon tetrachloride, carbon dioxide, and dry chemical agents of the bicarbonate of soda type. Its high dielectric strength makes it suitable for use on electrical fires, and it leaves no residue. Toxicity studies have shown Freon itself to be least toxic of various chemical extinguishing agents currently in use. However, at elevated temperatures Freon forms toxic decomposition products. Its mechanism of action appears to be extinguishment through a chemical reaction with combustion products, which process stops flame propagation. The use of the product as an aircraft power plant extinguishing agent is a practical application and illustrates this particular mechanism. Studies on other halogenated hydrocarbons as potential fire extinguishing agents are in progress (18, 31).

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13. ABSTRACT The problem of fire ignition and flame propagation in oxygen-containing or oxygen-enriched environments is dependent upon both the percentage of oxygen, oxygen partial pressure, and presence of the diluent inert gas. Oxygen percentage is the single most important feature and its effect is most strikingly greater than 42 per cent. The diluent gas affects the initial combustion temperature and the rate of propagation. Helium requires a higher ignition temperature, but produces an increased spread; while nitrogen requires a lower ignition temperature, but shows a decreased propagation rate. The most effective extinguishment system employs a hand-held, high-pressure, water hose. However, specific prevention measures are mandatory when dealing with these environments.			

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